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17.2 LLNL Energetic Materials Stability Review Program

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Recommended for approval by the ES&H Working Group

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New document or new requirements

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17.2

LLNL Energetic Materials Stability Review Program*

Contents

Terms and Definitions ii

1.0 Introduction 1
- 1.1 Purpose and Scope 1
- 1.2 General Requirements 1

2.0 Hazards 2

3.0 Controls for Working with Stabilized Energetic Materials 3
- 3.1 Stability Review Interval 3
- 3.2 Stability Review Date 5
- 3.3 Modification of the Stability Review Interval and Date 6
- 3.4 Bulk Propellants Surveillance 7
- 3.5 Stabilizer Threshold Values 8
- 3.6 Desensitized Energetic Materials 9

4.0 Responsibilities 9
- 4.1 Custodian 9
- 4.2 Owner 10
- 4.3 Synthesizer or Formulator 10
- 4.4 Explosives Handlers 11
- 4.5 Site 300 Controlled Materials Group 11
- 4.6 Hazards Control Explosives Safety 11
  - 4.6.1 Hazards Control Explosives Safety Technical Leader 11
  - 4.6.2 ES&H Team Explosives Safety Engineers 12
- 4.7 Energetic Materials Program Element Leader 12
- 4.8 LLNL Explosives Safety Committee 12
  - 4.8.1 Committee Chair 12
  - 4.8.2 Committee Personnel 12
- 4.9 Supervisors and Managers 13

5.0 Work Standard 13

6.0 Resources for More Information 13
- 6.1 LLNL Contacts 13
- 6.2 Other Sources 13

Appendix A Explosives Safety Data Form 14

* Minor revision

Terms and Definitions

Custodian	The person having custody or control of the energetic material in storage.
Energetic materials database report	A listing of stabilized energetic materials by lot number, with their assigned Stability Review Interval and Stability Review Date, as well as other information on the materials.
Owner	The person to whom the explosive material or explosive device is assigned. The owner is ultimately responsible for ensuring that all materials that require a stability review interval have a current stability review date. Every explosive material or explosive device shall have an owner.
Stability review interval	The period of time allowed between stability tests for a given lot of material.
Stability review date	The date by which a given lot of material shall be retested for stability. This date is obtained by adding the Stability Review Interval to the date of manufacture (DOM) or to the date of the most recent stability testing.
Synthesizer or formulator	Any person who synthesizes or formulates energetic materials.

17.2

LLNL Energetic Materials Stability Review Program

1.0 Introduction

1.1 Purpose and Scope

Some energetic materials, particularly nitrate-ester-based (e.g., nitrocellulose and nitroglycerine) propellants and explosives, contain stabilizers to control the decomposition rate of the nitrate esters. These materials are stabilized at the time of manufacture with ingredients that react with the nitrogen oxide decomposition products. However, as the level of stabilizer diminishes over time to the point that it can no longer consume the decomposition products, the decomposition rate may accelerate and may in certain cases produce spontaneous ignition through self-heating. An increase in the decomposition rate may also cause energetic materials to become more sensitive to initiation stimuli, thus making them more hazardous to handle, store, or transport. Consequently, the Laboratory has established the Energetic Materials Stability Review Program to monitor the level of stabilizer in these materials. The primary objective of the program is to ensure safe storage of the Laboratory's inventory of stabilized energetic materials, including nitrate-ester-based gun propellant, whether they are loaded in ammunition, articles, or sub-components, or stored in bulk configuration. The program is also designed to ensure timely use or disposal of energetic materials to prevent inadvertent use of those that have degraded.

This document supersedes portions of the previous *Explosives Handling and Stability Review Interval Program at LLNL* (UCRL-ID-120263) that relate to the stability review of energetic materials. It contains requirements for compliance with LLNL's Energetic Materials Stability Review Program as well as the responsibilities of individuals and organizations with regard to handling, testing, and storing nitrate-ester-based energetic materials.

Explosives handlers shall be familiar with and adhere to the requirements in this supplement and their responsibilities for working with stabilized energetic materials. Supervisors and managers also shall be familiar with the requirements and properly apply them to their energetic materials operations.

1.2 General Requirements

Following are the Laboratory's general requirements for stabilized energetic materials. Exceptions to the procedures in this document may be granted by the Energetic

Materials Program Element (EMPE) leader, with concurrence of the Hazards Control Explosives Safety technical leader.

- A stability review interval shall be established for all energetic materials containing stabilized nitrate esters in concentrations greater than 4% by weight, including all batches or lots. A stability review interval is also needed for all components and devices made with these energetic materials, except small-arms ammunition and Form 4 explosives-contaminated waste.
- A stability review interval also may be established for materials containing unstabilized nitrate esters that normally would contain a stabilizer or for other materials whose stability, as it relates to safety in storage, may be in question.
- The stability review interval shall be used to assign a stability review date to all lots of energetic materials or devices and articles containing such materials. The assigned stability review interval defines how often the stabilizer content of the material is monitored and tested. If the stability review date is exceeded, Hazards Control Explosives Safety shall be notified. The material shall be isolated in storage and further handling and transportation shall be restricted only to that necessary for evaluating its stability characteristics or for disposal.
- The stability review interval shall be established based on the control requirements in Section 3.0. Because each energetic material has its own unique stability properties, standardized stabilizer levels and testing are not applicable.

2.0 Hazards

Following are the known hazards associated with the stability of nitrate-ester-based energetic materials.

- The decomposition rate of nitrate-ester-based energetic materials may, in certain cases, produce spontaneous ignition through self-heating if the stabilizer has been depleted.
- An increase in the decomposition rate may cause nitrate-ester-based energetic materials to become more sensitive to initiation stimuli, thus making them more hazardous to handle, store, or transport.

3.0 Controls for Working with Stabilized Energetic Materials

The controls required for work with stabilized energetic materials are listed in the subsections below. Specific responsibilities are identified in Section 4.0.

3.1 Stability Review Interval

- The Energetic Materials Database Report, maintained by Hazards Control Explosives Safety, contains the stability review date for stabilized energetic materials that have been tested. If the stability review date for an energetic material is not listed in this report, the owner shall initiate the process shown in Fig. 1.
- When an energetic material containing stabilized nitrate esters in concentrations greater than 4% by weight is produced under a peer-reviewed procedure, the stability review interval (if required) shall be specified in that procedure.
- When a new energetic material containing stabilized nitrate esters in concentrations greater than 4% by weight is received onsite, the stability review interval will be established and listed on the Explosives Safety Data Form (Appendix A) and added to the Energetic Materials Database Report.
- If an explosive is new to LLNL, but other Department of Energy (DOE) contractors or Department of Defense (DoD) agencies have extensive experience with that material, any information received from these agencies may be used; however, the assignment of a stability review interval shall be conservative.
- Energetic materials for which LLNL personnel have much information or experience should be assigned a stability review interval commensurate with that information or experience.
- For commonly available commercial gun propellants (e.g., IMRs, H870), the manufacturers' suggested shelf life will be the assigned stability review interval, with approval of the EMPE leader and concurrence of the Hazards Control Explosives Safety technical leader. It is up to the owner of the material to obtain the shelf-life information if he/she wishes to use this data to assign the stability review interval.
- The stability review interval for articles, components, or pressed billets and parts made from bulk material or molding powder shall be the same as that for the original source material. The stability review interval for formulations shall be the same as that for source materials having the shortest interval.

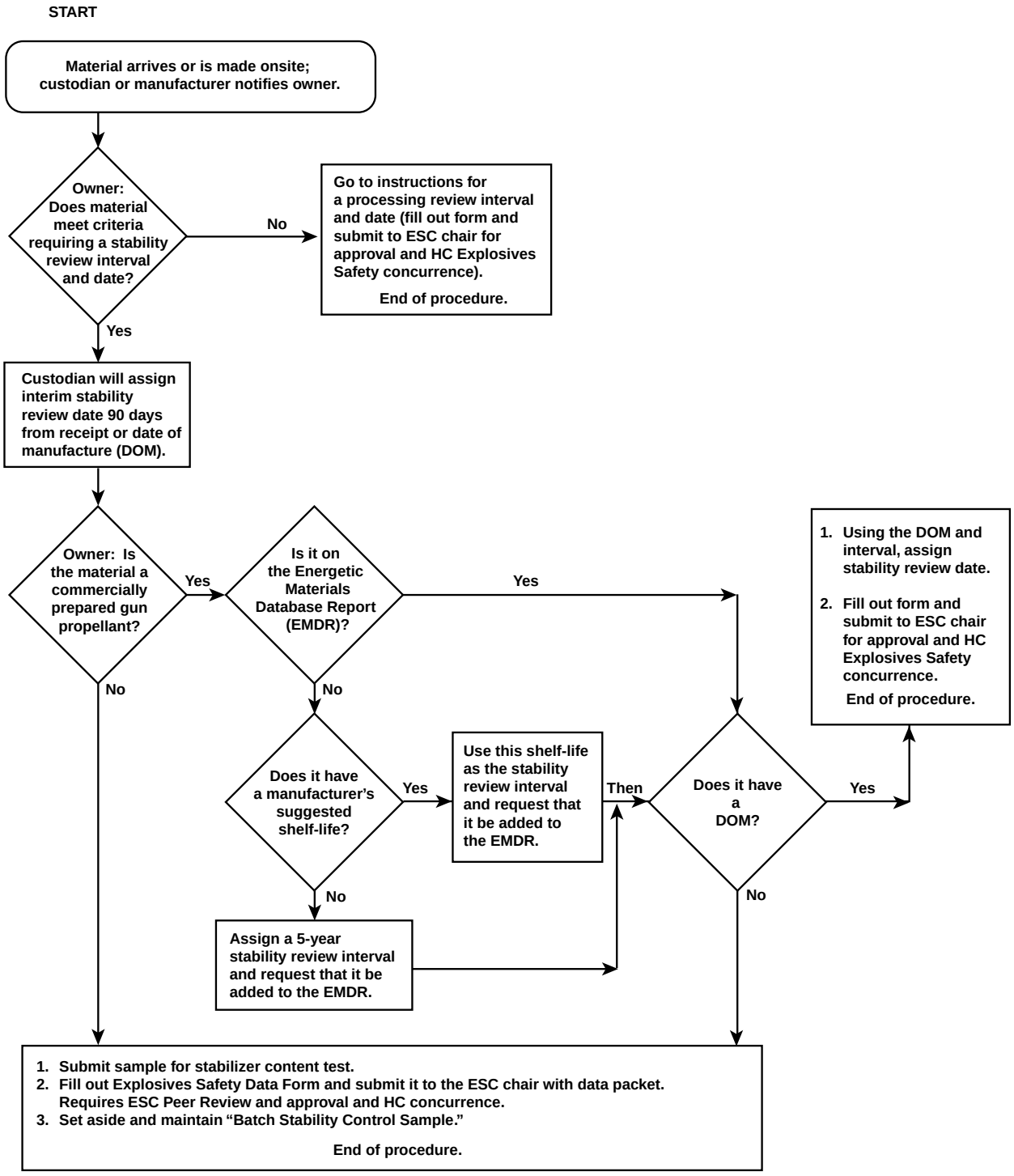

Figure 1. Overall scheme of the procedure for assigning stability review intervals and stability review dates.

3.2 Stability Review Date

- The stabilizer content for the energetic material must be known before a stability review date can be assigned. (This requirement does not apply to commercially produced gun powders when the date of manufacture is used to assign the stability review date.) The default date is 90 days from the date the material arrives onsite or the date of manufacture for materials produced onsite. A case-by-case review will be required to use materials during the interim period between their arrival onsite and the time the stabilizer content has been determined.
- The stability review date is determined by adding the stability review interval to the date of manufacture, if known, or to the latest stability test date, whichever is later.
- If the date of manufacture for the material cannot be determined, applicable stability tests will be performed and the results submitted to the appropriate peer reviewers of the Explosives Safety Committee (ESC). The peer reviewers, with concurrence from Hazards Control Explosives Safety, will assign the stability review interval and date based on the test data submitted. Where there is uncertainty about extending the stability review date for a given material, the EMPE leader and Hazards Control Explosives Safety technical leader shall be consulted for guidance.
- The stability review date for pressed billets, parts made from molding powder, and cast or extruded parts will be the same as that of the original source material.
- The stability review date for a mixture or blend (formulation) of two or more energetic materials shall be the same as that for the material with the earliest stability review date. However, if testing shows the formulation to be less stable than the least stable component, a shorter interval and a closer new date shall be established.
- When applicable, the stability review date shall be on or adjacent to the identification tag or on the explosives identification label on every container or package of energetic materials in use or in storage. For energetic materials that do not require a stability review interval, the term "N/A" (not applicable) shall be entered on the form or label in the place where it requests a stability review date.
- Stabilized energetic materials in storage that have no stability review date, or whose review date cannot be traced to the original source material, shall be assigned a date 30 days after the materials are discovered. Testing also shall be done during this time period to determine the stabilizer content. A new

date can then be established based on the test data. A case-by-case review will be required to use materials during the 30-day period prior to determining the stabilizer content.

- As a general rule, all materials shall be submitted for testing at least 30 days before the stability review date. This should be sufficient time for the owner of the material to obtain the stabilizer content of the material.

3.3 Modification of the Stability Review Interval and Date

- The stability review interval for each material will generally not be modified. If new data indicate that an existing interval is either too long or too short, the stability review interval may be modified by the ESC Peer Reviewers, with concurrence from Hazards Control Explosives Safety and approval by the ESC Chair. Modification of a stability review interval will be logged into the Energetic Materials Database Report maintained by Hazards Control Explosives Safety. Modification of the stability review interval will generally apply to all lots or batches of that material.
- The stability review date for a material may be extended by lot or batch. Extension of the stability review date does not apply automatically to other lots or batches that may have the same stabilizer, but may be granted if sufficient information has been obtained to warrant it.
- To extend a stability review date, the amount of stabilizer remaining in a sample of each lot or batch shall be quantitatively measured. Various techniques [e.g., high-performance liquid chromatography (HPLC)] are acceptable, but shall be approved by the EMPE Leader. The ESC Peer Reviewers, in consultation with Hazards Control Explosives Safety, shall review the new stabilizer content data to determine if the stability review date should be extended; the ESC Chair gives final approval. Modification of a stability review date will be logged into the Energetic Materials Database Report maintained by Hazards Control Explosives Safety. If the stability review date cannot be extended, more stabilizer should be added or the material should be destroyed.
- Purification of an energetic material may result in a new stability review date for an explosive if the stabilizer level is re-established. In such cases, the date of purification becomes the new date of manufacture and the stability review interval remains the same.
- Energetic materials may be disposed of in lieu of performing the required stability tests. However, this should occur before expiration of the stability review date to assure safe disposal.

CAUTION

- Explosives or devices containing energetic materials with an expired stability review date shall not be removed from storage, except in the following situations:
  - — To place the explosive or device in segregated storage.
  - — To obtain a sample of the material for stability testing. (Note: Only the minimum amount needed for the test shall be forwarded to the testing laboratory. The label and shipping tag shall be marked "For Safety Tests Only.")
  - — For onsite disposal.
- If there is a need to use energetic materials whose stability review date has expired without testing, an ESC peer review shall be conducted and the conditions for use shall be approved by the EMPE leader, with concurrence of the Hazards Control Explosives Safety technical leader. If new hazards and controls are identified, an Operational Safety Plan (OSP) will be required.

3.4 Bulk Propellants Surveillance

For bulk propellants in storage, it is advisable to perform an annual screening test using methyl violet paper to determine if there is formation of NO_X. If a color change is observed on the methyl violet paper, a quantitative measurement should be taken promptly to determine the amount of the remaining stabilizer in the propellant. The results of the test will determine the appropriate steps necessary (see Section 3.5).

To check each container to determine if there is NO_X, the following steps are required:

1. Place a one-tenth normal methyl violet test strip in each container. Using a pencil, mark the date on the test strip before placing it in the container.
2. Each year, 20 percent (rounded up to the next whole number) of the containers in each lot shall be selected and the test strip examined. A previously checked container shall not be examined again until all containers in the lot have been inspected in the current cycle. (This check is authorized to be performed in the magazine if it is not necessary to remove nails or screws to open the container. Otherwise, the work shall be performed in an approved explosives work area.)
   - If the color of the methyl violet test strip has bleached or changed to white, this indicates that NO_X may be present and the explosive is considered to be in the process of autocatalytic breakdown. In such case, take the following actions:
     - — Immediately notify Hazards Control Explosives Safety and the ESC chair.

  - Immediately reclassify all energetic materials of the same lot number as Storage Compatibility Group "L" and move to appropriate storage.
  - Inspect the methyl violet test strips in all containers.
  - Submit a sample from each lot having a bleached test strip for a quantitative measure of remaining stabilizer and take appropriate actions for the test results obtained.

- If the color of the methyl violet test strip did not change,
  - Insert a new dated test strip into the container and reseal the container.
  - Clearly mark each inspected container to indicate that it has been checked in the current cycle.

3.5 Stabilizer Threshold Values

- A stabilizer threshold value shall be quantitatively determined for each material and lot using techniques such as HPLC or thin-layer chromatography (TLC) and shall be listed in the Energetic Materials Database Report. This value will be the lower of 30 weight percent of the initial stabilizer content or 0.2 weight percent of the total material in the formulation that requires stabilizer.
- Some stabilizers have decomposition products that are themselves stabilizers and are sometimes more effective than the original material. The stabilizing effect of these daughter products may be taken into account by peer reviewers when determining the effective stabilizer content of a material. See the Department of Navy procedures (SW020-AE-SAF-010) referenced in Section 6.2 for detailed guidance on determining the effective stabilizer content of a material.
- When the stabilizer content of a material is above the threshold value, no action is required. If the stabilizer content is at or below the threshold value, notification of Hazards Control Explosives Safety and the following actions are required:
  - When the level of stabilizer is at or greater than 20% of the initial stabilizer content, add more stabilizer to the material (liquids) if possible or schedule the material to be used or disposed of within one year of the most recent stabilizer analysis.
  - If the level of stabilizer is below 20% of the initial stabilizer content, schedule the material to be used or disposed of within 30 days of the most recent stabilizer analysis. Change the Storage Compatibility Group of the material to "L" and store the material accordingly.

Note: Comparison of stabilizer content with the threshold value requires consideration of the accuracy of the measurement techniques and knowledge of initial stabilizer content.

3.6 Desensitized Energetic Materials

Energetic materials in a desensitizing volatile solvent or water may have a second stability issue: the possible loss of solvent or other liquid desensitizer. Therefore, control of the amount of desensitizer present is critical to safe handling of these materials. To be sure the level of desensitizer remains adequate, do the following:

- Visually check the level of solvent or other liquid desensitizer in each container annually. Replace any lost fluid. As an aid, mark the fluid level on the container and include the date at the time of storage.
- Quantitatively analyze the amount of desensitizer present during each stability review of liquid nitrate esters. If the level of desensitizer is below the acceptable amount, add more desensitizer.

4.0 Responsibilities

All workers and organizations shall refer to Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management" in the *ES&H Manual* for a list of general responsibilities. Specific responsibilities for individuals and organizations with key safety roles in the LLNL Energetic Materials Stability Review Program are listed below each title.

4.1 Custodian

- Notify owners 60 days in advance of the stability review date and testing due date for their energetic materials in storage. If the owner does not respond within 30 days, notify the ESC chair so that appropriate actions may be taken.
- Maintain a file of Explosives Safety Data Forms for all energetic materials in your custody that require stability review dates.
- Update labels on energetic materials in storage upon receipt of new Explosives Safety Data Forms.
- Comply with the requirements and guidance in Section 3.4 and 3.6 for materials in your custody.

4.2 Owner

- Determine whether a material requires a stability review interval and stability review date.
- Submit samples of material for stabilizer testing at least 30 days before the stability review date.
- Complete and send to the ESC chair for processing and approval the Explosives Safety Data Form to establish a new stability review interval and date for each new lot of material made or received onsite. This shall be done within 30 days of manufacture onsite (or receipt onsite) so that the stability review interval and date can be assigned within 90 days.
- Complete and send to the ESC chair for processing and approval a new Explosives Safety Data Form whenever a lot of stabilized material has been retested and needs a new stability review interval or date.
- Send custodians a copy of the Explosives Safety Data Form whenever a new stability review interval or date is established for materials in their custody.
- Maintain a Batch Stability Control Sample for each lot of pure explosive material requiring stability review as long as any of the original material or formulations, parts, or devices containing the material exist onsite. If any of these products is sent offsite for other than immediate use or disposal, a portion of the Batch Stability Control Sample should accompany the shipment.
- Pay all costs associated with stability testing and disposition of energetic materials containing stabilizers.
- Notify Hazards Control Explosives Safety soon after completing the tasks in Sections 3.4 and 3.5 if the stability test data show one or more of the following results:
  - NO_X is detected during bulk propellant surveillance with methyl violet paper.
  - Stabilizer content is at or below the stabilizer threshold value.

4.3 Synthesizer or Formulator

- Identify an owner for each batch of explosive material prepared.
- Assign a unique lot number to each batch of explosive material.
- Assign an initial stability review interval of 90 days to each new material or formulation. Notify the owner to start the process of obtaining a stability review interval and date for the material.

- For a newly synthesized explosive that will require review, establish an appropriate schedule for stability testing for the projected life of the explosive. Take a sample from each batch and identify it as the Batch Stability Control Sample.
- Provide the Batch Stability Control Sample to the owner of the material.

4.4 Explosives Handlers

Explosives handlers shall not use materials whose stability review date has expired. See Section 3.3 for exceptions.

4.5 Site 300 Controlled Materials Group

- Assign an interim stability review date 90 days from the date a material is first received onsite. Notify the owner to start the process of obtaining a stability review interval and date.
- Update the inventory database and labels on energetic materials upon receipt of new Explosives Safety Data Forms.
- Ensure that shipments of energetic materials shipped between sites or offsite, or to organizations outside EMPE onsite, have current stability review dates. This requirement does not apply to samples sent for stability testing or for onsite disposal or onsite treatment.
- Perform the custodian duties in Section 4.1, as applicable.

4.6 Hazards Control Explosives Safety

4.6.1 Hazards Control Explosives Safety Technical Leader

- Consult with the EMPE leader and provide concurrence with any exceptions to the procedures described in this document.
- Consult with the EMPE leader and provide concurrence with assigning the stability review interval of commercial gun propellants based on the manufacturer's suggested shelf life.
- Consult with the EMPE leader and provide guidance where uncertainty exists for extending the stability review date for a given material.
- Ensure that an Energetic Materials Database is maintained and the report is available to those who may request it.

4.6.2 ES&H Team Explosives Safety Engineers

- Review and concur with completed Explosives Safety Data Forms.
- Prepare and distribute appropriate notifications to all affected owners, custodians, and the Site 300 Manager when stability test results indicate that a material should be destroyed or used within one year or less.

4.7 Energetic Materials Program Element Leader

- Consult with the Hazards Control Explosives Safety technical leader and provide the following:
  - — Approval for any exceptions to the procedures described in this document.
  - — Approval for assigning the stability review interval for commercial gun propellants based on the manufacturer's suggested shelf life.
  - — Guidance where uncertainty exists for extending the Stability Review Date for a given material.
- Approve the tests to be used for determining the stability of energetic materials.
- Approve the tests to be used for quantitative analysis of the stabilizer and the oxidation products in energetic materials.
- Maintain the file of all original Explosives Safety Data Forms.

4.8 LLNL Explosives Safety Committee

4.8.1 Committee Chair

- Approve peer-reviewed Explosives Safety Data Forms after obtaining concurrence from Hazards Control Explosives Safety.
- Distribute copies of the completed and signed Explosives Safety Data Forms to Hazards Control Explosives Safety, the owner, and the Site 300 Controlled Materials Group. Submit the original copy to the EMPE Section for retention.

4.8.2 Committee Personnel

- Determine the appropriate tests to detect decomposition and measure stabilizer content.
- Review newly established stability review intervals and dates.
- Review extensions of stability review dates.
- Determine the stabilizer threshold values.

4.9 Supervisors and Managers

- Implement the LLNL Energetic Materials Stability Review Program.
- Establish a system to assess compliance with the program.
- Provide workers training on the requirements of the program.

5.0 Work Standard

DOE M 440.1-1, *DOE Explosives Safety Manual* .

6.0 Resources for More Information

6.1 LLNL Contacts

For additional information regarding this document, contact the following:

- Chemistry & Materials Science Energetic Materials Program Element (EMPE) leader.
- LLNL Explosives Safety Committee chair or the members.
- Hazards Control Explosives Safety technical leader.
- ES&H Team Explosives Safety engineer.
- Site 300 Controlled Materials Group.

6.2 Other Sources

Establishment of a Safe Interval Prediction and a Modified Time-To-Fume Test, Technical Report, ARAED-TR-96019, U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, New Jersey (August, 1996).

Propellant and Propelling Charges Ammunition Surveillance Procedures, SB 742-1300-94-895, Department of the Army (March 7, 1995).

Safety Surveillance of Navy Gun Propellant, Policy and Procedures, SW020-AE-SAF-010, Department of the Navy (September 23, 1996).

Sandia Explosives Safety Manual, Appendix G, "Storage Review Matrices," Sandia National Laboratories (August 1996).

Appendix A

Explosives Safety Data Form

Part I. General Information

Owner_____**Explosive ID and LLNL Lot #**_____
Manufacturer_____
Manufacturer's designation_____
UNO Hazard Class/Division_____**SC/HC Group**_____
DOT reference number_____
IHC (if applicable) and expiration date_____
Composition or chemical name_____
Date manufactured_____**Date received by LLNL**_____
Explosive components and their Processing and/or Stability Review Dates_____
Mfg.'s recommended shelf life_____
Physical state: (solid/liquid, m.p., b.p., etc.)_____
Color_____

Part II. Stability Information

Stabilizer_____ **Original Manufactured Stabilizer Wt%**_____
% Effective Stabilizer_____
ASSIGNED STABILITY REVIEW INTERVAL_____
ASSIGNED STABILITY REVIEW DATE_____

Part III. Sensitivity Information

Sensitivity: **DSC exotherms (attach curves)**
Chem. Reactivity Test (CRT)_____**cm3/g@**_____**°C for** _____**hr.**
Impact 2.5 kg **Type 12** **Type 12B**
Sample_____
Control_____
Spark_____
Friction_____
Other_____
Precautions: **Toxicity**_____
Compatibility_____
Protective equipment_____
Other_____
ASSIGNED PROCESSING REVIEW INTERVAL_____
ASSIGNED PROCESSING REVIEW DATE_____

Explosives Safety Committee Peer Review **Concurrence:**_____
Group I_____ **Hazards Control Explosives Safety**
Group II_____
Group III_____ **Approval:**_____
Explosives Safety Committee Chair

Distribute copies to: Owner/Consignor, Hazards Control Explosives Safety, and Site 300 Controlled Materials Group. Original to be retained by Energetic Materials Program Element master file.